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THE UNIVERSITY OF OKLAHOMA

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VIBRATIONALLY INELASTIC SCATTERING AT MODERATE ENERGIES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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VIBRATIONALLY INELASTIC SCATTERING

AT MODERATE ENERGIES

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CHAPTER I

INTRODUCTION

The transfer of energy from translation to internal states of molecules during collisions plays an essential role in numerous molecular processes. For example, collisional excitation of vibrational and rotational energy levels is a major mechanism by which population inversions are produced in chemical lasers[1] and by which molecular reactants acquire the activation energy by which to form new products.[2]

Crossed molecular beam techniques are now beginning to yield detailed information concerning the outcome of inelastic molecular collision events.[3] The output of such experiments is in the form of angular distributions and cross sections. Thus we now have microscopic experimental techniques to compare with theoretical collision dynamics, whereas previously experiments were concerned with bulk properties for collisions in gases, such as relaxation times, transport properties, etc.

The theoretical description proceeds by selection of a potential energy surface which describes the interaction between the collision partners. Rigorous theoretical, or ab initio methods to calculate reliable potential surfaces are difficult to apply and, as yet, there is

no direct method for inverting the process in order to determine the inelastic scattering potential from experimental measurements. However, new techniques are rapidly being developed which may facilitate the inversion process for the inelastic case.[4]

The next step involves the solution of the scattering problem to obtain the probabilities for the inelastic events which can take place in the system. The formal theory for molecular scattering has been developed[5] but exact calculations, although feasible, are usually difficult and time-consuming to perform. Therefore, various models of the collision process have been designed to replace an exact solution to the dynamics of a collision.[6,7]

The problem of vibrationally inelastic collisions which are energetic enough to produce vibrational transitions is a difficult one. Every system with vibrational levels will also have rotational energy levels which are closely spaced compared to the vibrational levels so that rotational transitions will occur for each vibrationally inelastic event. Approximations which can treat a few widely spaced levels will fail for the rotational part, while those valid for a large number of closely spaced levels will fail for the vibrational part.

The simplest model with which to treat this problem is a collinear collision of an atom with a diatomic molecule. This procedure eliminates the rotational part of the problem and the anisotropy of the vibration part of the interaction potential. The first exact classical calculation for this model was made by Kelley and Wolfsberg.[8] They used both harmonic and Morse oscillator potentials to describe the diatomic molecule along with an empirical interaction potential to obtain

the exact classical energy transfer. Recently, this classical model has been extended to two dimensions.[9] Secrest and Johnson[10] first calculated exact quantum mechanical transition probabilities in one dimension for an harmonic oscillator in soft collisions. These calculations have been extended to a Morse oscillator and several different systems.[11] By assuming that all the ignored orientations and impact parameters make a rapidly and regularly decreasing contribution to the inelastic scattering, a steric factor can be introduced to obtain a three-dimensional average transition probability. The steric factor is usually set equal to a constant[12] or obtained by some prescription.[13] The transition probability thus obtained can then be used to calculate relaxation rates for the system. The steric factor concept has been found to be generally invalid for vibrationally inelastic events.[12,14,15] Since cross sections are obtained by integrating over impact parameter, they cannot be obtained from this model.

At the other extreme, the rotational part of the problem may be removed when the rotational period is much shorter than the duration of the collision. The vibrating molecule is treated as a sphere which undergoes changes in radius as the molecule vibrates. This is the basis for the breathing sphere model.[16] Although such a model is not realistic, since there is no coupling of angular momenta for a spherical potential, it allows for a three-dimensional test for various other approximations.[17]

In the last few years a series of papers has introduced what are now called "effective Hamiltonian" techniques.[18-23] These approximate methods, which achieve a reduction in the number of coupled equations,

all involve various types of angular momentum decouplings. The reduction is effected by altering or eliminating states not directly measured. Rabitz[24] has indicated the flexibility in choice of an effective Hamiltonian with regard to computing time and accuracy requirements for two colliding molecules and for an atom-molecule collision. It has been pointed out[25] that with increasing anisotropy of the interaction potential the effective Hamiltonian methods are likely to become less adequate because they employ approximate angular momentum coupling.

The above approximation methods appear to have general applicability to the classical, semi-classical and quantum mechanical formulations for inelastic collision probabilities. For example, Augustin and Rabitz[27] have extended the effective Hamiltonian methods to the classical S-matrix theory.

A completely classical S-matrix formulation of a molecular collision problem has been proposed by Miller.[26] He showed how to construct the classical limit of a quantum mechanical S-matrix by exact numerical solution of the classical equations of motion. Quantum mechanics is introduced into this theory by the superposition principle whereby probability amplitudes are added instead of the probabilities themselves. The method has been extended to those processes which are classically forbidden by a partial averaging technique which treats, for example, rotation by a Monte Carlo averaging and vibration by classical techniques. This classical model requires a root searching procedure to determine classically-allowed trajectories and complex value trajectories for classically-forbidden trajectories. Doll and Miller[43] have applied this method to investigate various three-dimensional atom-

diatom collisions, and compared their results with the quantum mechanical calculations of Eastes and Secrest[29] for collision energies in a range of 1-2eV, and obtained excellent agreement.

An exact quantum mechanical result means a close coupling calculation.[28] In practice the expansion of the total wave function in terms of complete sets of basis functions must be truncated to a finite number of basis functions. This is done by adding functions until a prescribed convergence criterion is reached. Close coupling calculations in three dimensions are scarce. To date, few atom-diatomic molecule system calculations have been made which include both vibrational and rotational states. Those that do carry only two or three rotational channels.

While the previous two formulations have described the collision system degrees of freedom either entirely classically or entirely quantum mechanically, it is possible to use a mixed description. The semiclassical formulation treats the inelastic scattering as a time-dependent perturbation on the internal coordinates while the relative coordinates follow a trajectory determined by a spherically symmetric potential. This method has been used in a first-order perturbation treatment and a multiquantum treatment of collinear scattering by empirical potentials.[30,31] The time-dependent formalism was extended to three dimensions by invoking the breathing sphere model[33] for an energy range below one-half eV.

Another formulation for semi-classical inelastic scattering has been developed and applied to three-dimensional, vibrationally inelastic collisions in the sudden approximation.[34-38] This method will be

described in detail in the next chapter, where modifications will be made in order to describe inelastic events at moderate collision energies.

The sudden approximation provides a simple high energy limit from which one can obtain probabilities and cross sections for inelastic transitions with an effort consistent with the presently limited knowledge of intermolecular interaction potentials. It would be valuable to have an equally simple method for describing inelastic events at moderate collision energies -- from about 4eV up to the sudden limit.

We propose to develop a rather simple semi-classical approach for taking into account deviations from the sudden approximation while maintaining at the same time the calculational facility of the sudden limit. We will account for vibrational energy level differences by relaxing the sudden approximation with a constant energy-level spacing between the initial vibrational state and all possible final states. A prescription for choosing this spacing will be based on an exact collinear quantum mechanical calculation. We then extend the formulation to three dimensions and compare the result with that obtained in the sudden approximation for the same collision processes.

CHAPTER II

THEORETICAL FORMULATION OF THE SCATTERING PROBLEM

1. Formal Theory

The formal theory of scattering states that a collision process may be sufficiently described by the stationary solutions, $\psi(\underline{r},\underline{R})$, of the time-independent Schrodinger wave equation:

$$[\, H_1 + H_2 - (\hbar^2/2\mu)\nabla^2 + V_o(\underline{r}) - E \,]\psi(\underline{r},\underline{R}) = -\Delta V\psi(\underline{r},\underline{R}). \qquad (2.1)$$

Here, H_1 and H_2 are the Hamiltonians of noninteracting collision partners, $\underline{r}$ is a vector joining the centers of mass of the molecules, and $\underline{R}$ represents the collective internal coordinates. The interaction potential, $V(\underline{r},\underline{R})$, has been written as the sum of a spherically symmetric part, V_o, and a part, ΔV, which contains the dependence on the internal coordinates of colliding systems. In writing Eq. (2.1), we must make two assumptions: (i) electron transitions are ignored; and (ii) the process is limited to energies below the threshold for dissociation of the collision partners so that we will not consider the continuum.

We reduce Eq. (2.1) to a set of coupled second-order ordinary differential equations by expanding ψ in terms of the eigenfunctions ϕ_{1n} and ϕ_{2n} of H_1 and H_2, respectively:

$$\psi(r,\theta,\phi) = \sum_{n\ell m} r^{-1} u_{n\ell m}(r) Y_{\ell m}(\theta,\phi)\phi_{1n}\phi_{2n} \qquad (2.2)$$

where ℓ and m are the orbital quantum numbers associated with state n

and the $u_{n\ell m}(r)$ are as yet undetermined radial wave functions. The index n represents all of the internal quantum numbers. Putting Eq. (2.2) into Eq. (2.1) yields

$$\left[(d/dr)^2 - \ell(\ell+1)/r^2 + k_n^2 - U_o(r) \right] \sum_{n\ell m} u_{n\ell m} Y_{\ell m} \phi_{1n} \phi_{2n} = \Delta U \sum_{n\ell m} \phi_{1n} \phi_{2n}, \tag{2.3}$$

where

$$U_o(r) = 2 V_o(r)/\hbar^2$$

$$\Delta U = 2\mu \Delta V/\hbar^2$$

$$k_n^2 = 2\mu(E - E_{1n} - E_{2n}).$$

μ is the reduced mass of the system, E the total energy, and E_{1n} and E_{2n} are the respective energy eigenvalues of H_1 and H_2. Both sides of Eq. (2.3) may be multiplied by $Y^*_{\ell',m'}, \phi^*_{1n}, \phi^*_{2n}$, and integrated over $\underline{R}$, θ, and ϕ to give

$$\left[(d/dr)^2 - \ell(\ell+1)/r^2 + k_n^2 - U_o(r) \right] u_{n'\ell'm'} = \sum_{n\ell m} U_{n'\ell'm'n\ell m} u_{n\ell m}, \tag{2.4}$$

where

$$U_{n'\ell'm'n\ell m} = \int \phi^*_{1n'} \phi^*_{2n'} Y^*_{\ell'm'} \Delta U \phi_{1n} \phi_{2n} Y_{\ell m} d\Omega d\underline{R} \tag{2.5}$$

Using the substitution

$$P_n^2(r) = k_n^2 - \ell(\ell+1)/r^2 - U_o(r) \tag{2.6}$$

we can write Eq. (2.4) in the more compact form,

$$u_n''(r) + p_n^2(r) u_n(r) = \sum_{n'} U_{nn'}(r) u_{n'}(r) \tag{2.7}$$

with n denoting the entire collection of indices. If ΔV vanishes, Eq. (2.7) reduces to a set of decoupled equations which describe elastic scattering.

2. Semi-classical Approximation

In order to describe the radial functions $u_n(r)$, we treat the three-dimensional collision process with the semi-classical methods developed by Cross.[33-38] These are based upon two mathematical approximations: the removal of rapid oscillations and the WKB approximation; the former requires the energy differences between the internal states to be small compared to the kinetic energy of the system and the latter requires that the deBroglie wavelength must be small compared to the range of the potential. The derivation then allows for a description in terms of classical trajectories and correctly predicst the asymptotic properties of interest such as probabilities and cross sections.

We begin the semi-classical treatment by writing the radial wavefunctions in terms of two linearly independent approximate solutions for elastic scattering from the spherically symmetric part of the potential. Then

$$u_i(r) = X_i(r)u_{1i}(r) + Y_i(r)u_{2i}(r). \tag{2.8}$$

Since Eq. (2.8) involves twice as many functions as Eq. (2.7), we may impose the following restrictions on the coefficients X_i and Y_i:

$$X_i'(r)u_{1i}(r) + Y_i'(r)u_{2i}(r) = 0 \tag{2.9}$$

Inserting Eq. (2.8) and (2.9) into (2.7) results in two sets of first-order coupled differential equations for the X_i and Y_i. These are

$$X_i' = \sum_j (A_{ij}X_j + B_{ij}Y_j) \qquad (2.10a)$$

and

$$Y_i' = \sum_j (C_{ij}X_j + D_{ij}Y_j),$$

where

$$A_{ij} = W_i^{-1}(u_{2i}u_{1i}'' + P_i^2 u_{2i}u_{1i})\delta_{ij} - W_i^{-1}u_{2i}U_{ij}u_{1i} , \qquad (2.11a)$$

$$B_{ij} = W_i^{-1}(u_{2i}u_{2i}'' + P_i^2 u_{2i}u_{2i})\delta_{ij} - W_i^{-1}u_{2i}U_{ij}u_{2j} , \qquad (2.11b)$$

$$C_{ij} = W_i^{-1}(u_{ij}u_{ij}'' + P_i^2 u_{1i}u_{1i})\delta_{ij} + W_i^{-1}u_{1i}U_{ij}u_{1j} , \qquad (2.11c)$$

$$D_{ij} = W_i^{-1}(u_{1i}u_{2i}'' + P_i^2 u_{1i}u_{2i})\delta_{ij} + W_i^{-1}u_{1i}U_{ij}u_{2j} , \qquad (2.11d)$$

and W is the Wronskian of u_1 and u_2. The exact solutions of the elastic Schrodinger equation satisfy $u'' = -P^2u$, in which case the first terms of Eq. (2.11) are zero. Since u_1 and u_2 are approximate solutions for the elastic case we expect the first terms of Eq. (2.11) to be samll, and omit them from the following.

Outside of the classically-forbidden region and well away from a classical turning point, we can use simple WKB functions for u_1 and u_2. These are given by

$$u_{ij} = P_i^{-\frac{1}{2}} \exp(is_i - i\pi/4), \qquad r > r_{ci} \qquad (2.12a)$$

$$u_{2i} = P_i^{-\frac{1}{2}} \exp(-is_i - i\pi/4), \qquad r > r_{ci} \qquad (2.12b)$$

$$u_{1i} = u_{2i} = 0, \qquad r < r_{ci} \qquad (2.12c)$$

with

$$s_i = \left| \int_{r_{ci}}^{r} P_i(r')dr' \right| . \qquad (2.13)$$

The quantity $P_i(r)$ is the momentum associated with position r and r_{ci} is the classical turning point for the i^{th} state, i.e., the value for which $P_i(r_{ci}) = 0$. Equations (2.11) become

$$A_{ij} = -\tfrac{1}{2}\, i(P_i P_j)^{-\frac{1}{2}}\, U_{ij} \exp(-is_i + is_j), \tag{2.14a}$$

$$B_{ij} = -\tfrac{1}{2}\, i(P_i P_j)^{-\frac{1}{2}}\, U_{ij} \exp(-is_i - is_j), \tag{2.14b}$$

$$C_{ij} = \tfrac{1}{2}\, i(P_i P_j)^{-\frac{1}{2}}\, U_{ij} \exp(is_i + is_j), \tag{2.14c}$$

$$D_{ij} = \tfrac{1}{2}\, i(P_i P_j)^{-\frac{1}{2}}\, U_{ij} \exp(is_i - is_j). \tag{2.14d}$$

For the energy range we are concerned with, $P_i(r)$ is large so s_i is also large and varies rapidly with r. Thus, the B and C terms will be rapidly oscillating functions of r so that any integral over them will be negligible. The properties of U_{ij} are also important to the validity of this approximation: the U_{ij} must be sufficiently slowly-varying functions so that the average of

$$(P_i P_j)^{-\frac{1}{2}}\, U_{ij} \exp[\pm i(s_i + s_j)]$$

is close to zero. With only the slowly oscillating terms A and D remaining, we have the coupled equations

$$X_i' = \sum_j A_{ij} X_j \tag{2.15a}$$

and

$$Y_i' = \sum_j D_{ij} Y_j \quad . \tag{2.15b}$$

The neglect of the B and C terms means that we have lost quantum interference between the outgoing half of the trajectory represented by X_i and the incoming half represented by Y_i.

For energies in the range of a few electron volts, we expect only small relative changes in the relative energy transferred, since energy level spacings are on the order of one-half electron volt. Also, for most molecular collisions the angular momentum $\ell \approx 200$ and the changes $\Delta\ell$ are on the order of 10 or so.[39] Therefore, with $\Delta k/k$ and $\Delta\ell/\ell$ small, we can expand $(s_i - s_j)$ in a double Taylor series and retain only the first-order terms,

$$(s_i - s_j) \approx (\partial s/\partial k)(k_i - k_j) + (\partial s/\partial \ell)(\ell_i - \ell_j). \qquad (2.16)$$

The classical trajectory determined by $V_o(r)$ is specified by r, θ, and ϕ as functions of the time t. They are related by

$$dr = \mp P_o \hbar dt/\mu \qquad (2.17a)$$

and

$$d\theta = \pm \ell dr/r^2 P_o \ , \qquad (2.17b)$$

where the upper sign holds for the incoming half of the trajectory and the lower sign holds for the outgoing half.

In Eq. (2.17), we have an average momentum, P_o, to replace $(P_i P_j)^{\frac{1}{2}}$ which occurs in Eq. (2.14). We consider it to be an average P by which we can define a single classical trajectory. The manner by which such an average is defined has been shown to have little effect on the quantities calculated by its use. Substituting Eq. (2.17) into (2.16) yields,

$$(s_i - s_j) = \pm \omega_{ij}(t - t_c) \mp (\ell_i - \ell_j)(\theta - \theta_c) \ , \qquad (2.18)$$

where ω_{ij} is the energy difference between states i and j in units of $\hbar$. Substitution of Eqs. (2.17) and (2.18) into (2.15) effects a change-of-variables from r to t:

$$\dot{X}_i = -(i/\hbar)\sum_j V_{ij}\exp\left[\, i\omega_{ij}(t - t_c) - i(\ell_i - \ell_j)(\theta - \theta_c)\,\right]X_j \qquad (2.19a)$$

for $t \geq t_c$, and

$$\dot{Y}_i = -(i/\hbar)\sum_j V_{ij}\exp\left[\, i\omega_{ij}(t - t_c) - i(\ell_i - \ell_j)(\theta - \theta_c)\,\right]Y_j \qquad (2.19b)$$

for $t \leq t_c$. Continuity of the wave function requires that $X_i = Y_i$ at time t_c, the time at which the system is at the turning point.

As they stand, Eqs. (2.19) couple the vibrational, rotational, and orbital angular-momentum states of the colliding system. We now remove the orbital part by employing an action-angle transformation which is valid in the classical limit of large ℓ.[36] For large ℓ and $m \ll \ell$ we can use an asymptotic expansion of the spherical harmonic.[40]

$$Y_{\ell m}(\theta,\phi) \simeq \pi^{-1}(\sin\theta)^{-\frac{1}{2}}\cos\left[\, (\ell+\tfrac{1}{2})\theta - \pi/2 - m\pi/2\,\right]\exp(im\phi) \qquad (2.20)$$

which is valid for $\theta \gg 1/\ell$. The potential matrix can then be written as

$$V_{ij\ell'm'\ell m}(r) = (4\pi^2)^{-1}\int_0^{\pi} d\theta \int_0^{2\pi} V_{ij}(r,\theta',\phi')\exp(-i\Delta m\phi)$$

$$\cdot\left[\exp(i\Delta\ell\theta' + i\pi\Delta m/2) + \exp(-i\Delta\ell'\theta - i\pi\Delta m/2)\right]d\phi' \qquad (2.21)$$

where $\Delta\ell = \ell' - \ell$ and $\Delta m = m' - m$. Terms containing $\exp\left|\pm i(\ell+\ell')\theta\right|$ are highly oscillatory and are omitted. Making use of the fact that (θ',ϕ') and $(-\theta',\phi'+\pi)$ represent the same point in space, we can rewrite Eq. (2.21) as

$$V_{ij\ell'm'\ell m}(r) = (4\pi^2)^{-1}\int_0^{\pi} d\theta' \int_0^{2\pi} V_{ij}(r,\theta',\phi')\exp\left[\, -i\Delta m(\phi' - \pi/2)\right]$$

$$\cdot\left[\exp(i\Delta\ell\theta')d\phi'\right]. \qquad (2.22)$$

Since V as given by Eq. (2.22) depends on $\Delta\ell$ and Δm and not on indi-

vidual values of ℓ and m, we can diagonalize the orbital angular momentum via the transformation

$$X_i(t,\delta,\gamma) = (N_\ell N_m)^{-\frac{1}{2}} \sum_{\ell m} \exp\left[im(\gamma - \pi/2)\right]\exp(-i\ell\delta)X_{i\ell m}(t); \quad (2.23)$$

here, N_ℓ and N_m are the numbers of ℓ and m values respectively, to be used in the sum, and δ and γ are defined by

$$\delta = 2\pi n_\ell/N_\ell \ , \ \gamma = 2\ n_m/N_m \ . \quad (2.24)$$

As N_ℓ and N_m become large, X_i may be considered to become a continuous function of δ and γ. The inverse of Eq. (2.23) is given by

$$X_i(r,\ell,m) = (N_\ell N_m)^{\frac{1}{2}}(4\pi^2)^{-1} \int_0^{2\pi}\int_0^{2\pi} d\gamma\, d\delta \exp\left[-im(\gamma - \pi/2)\right] \cdot\left[\exp(i\ell\delta)X_i(r,\delta,\gamma)\right]. \quad (2.25)$$

Substitution of Eqs. (2.22) and (2.25) into (2.19a) yields

$$\dot{X}_i(t,\delta,\gamma) = -(i/\hbar)\sum_j V_{ij}(t,\delta + \theta - \theta_c,\gamma) \cdot\left\{\exp\left[i\omega_{ij}(t - t_c)\right]\ X_j(t,\delta,\gamma)\right\}. \quad (2.26)$$

By a similar procedure we obtain the coupled equations for Y_i. Equations of the form of (2.19) have been derived from time dependent perturbation theory by including the spherical harmonics in the original wave function. Transition probabilities can be obtained from the perturbation treatment, but the translational part is ignored so that angular distributions cannot be obtained. Equations similar to (2.26) have been used to describe vibrationally inelastic scattering in a collinear model.[30]

3. Treatment of Internal States by the Relaxed Sudden Approximation

The coupled equations still contain the rotational and vibrational transitions. The rotational dependence is removed by using the sudden approximation. Here, we assume that ω_{ij} does not depend upon rotational energy differences, i.e., that the energy-level spacing for rotational states is essentially zero. Further, we assume that remaining vibrational energy-level spacing contained in ω_{ij} does not depend upon the vibrational quantum numbers so that we can replace ω_{ij} by some constant value ω. We then have

$$\dot{X}_i(t,\delta,\gamma) = -(i/\hbar)\sum_j V_{ij}(t,\delta + \theta - \theta_c) \cdot\left[\exp\left[\, i\omega(t - t_c)\right] X_j(t,\delta,\gamma)\right] \tag{2.27}$$

with a similar expression for Y_i. We refer to this procedure as the "relaxed sudden approximation." At this stage it is not easy to assess the possible error introduced by the nature of this approximation. It has a strong appeal, in that it should permit a test of the usual sudden approximation which considers ω to be zero.

In the sudden approximation, the available energy levels are treated as if they are completely degenerate since the parameter ω expressing energy differences between states is set equal to zero. Under such a condition any classical path should be able to connect the appropriate internal states involved in an energy transfer during a collision. At low energies, however, this degeneracy should no longer be apparent to the colliding molecules and the sudden approximation should

fail.

As a next approximation, a constant, non-zero ω is chosen in order to closely reproduce the elastic scattering transition probability for an oscillator in its ground state as given by a quantum mechanical calculation for the collinear problem. Such a choice for ω makes all excited vibrational states degenerate, i.e., all excited states lie at the same energy above the ground state. Harmonic oscillator wave functions are then used to describe the internal vibrational states.

Equations (2.27) are still coupled to the various internal states by the potential matrix elements. The matrix elements have the form

$$V_{ij}(t) = \int \phi_i^*(\underline{R}) \Delta V \phi_j(\underline{R}) d\Omega \quad , \tag{2.28}$$

which represents a transformation from a basis set quantized in the set of quantum numbers i and j to a basis set in the internal coordinate representation. The basis set becomes a set of Dirac delta functions so that the inverse transformation is[33,34]

$$\sum_{ij} \phi_i(\underline{R})\, \phi_i |\Delta V| \phi_j\, \phi_j^*(\underline{R})$$

$$= \Delta V(\underline{R}) \delta(\underline{R}-\underline{R}') \quad , \tag{2.29}$$

where the closure property of the complete set of internal wave functions has been used. Using Eq. (2.29) we can diagonalize Eq. (2.27), producing the set of completely decoupled equations,

$$\dot{X}(t,\delta,\gamma,R) = -(i/\hbar)\Delta V(t,\delta + \theta - \theta_c,\gamma,R)$$

$$\cdot [X(t,\delta,\gamma,R)] \tag{2.30a}$$

for $(t \geq t_c)$ and

$$\dot{Y}(t,\delta,\gamma,R) = -(i/h)\Delta V(t,\delta + \theta - \theta_c,\gamma,R) \cdot [Y(t,\delta,\gamma,R)] \qquad (2.30b)$$

for $(t \leq t_c)$. The solution of Eq. (2.30) is obtained by a simple integration over the classical trajectory. For the asymptotic limit $r \to \infty$, we can write[41]

$$X(t \to +\infty) = \exp(2i\eta)\ Y\ (t \to -\infty) \qquad (2.31)$$

where the phase shift η is given by

$$\eta = -(2\hbar)^{-1} \int_{-\infty}^{+\infty} \Delta V \exp(i\omega t). \qquad (2.32)$$

The X and Y functions no longer depend upon the internal states of the collision partners, but they do depend upon the internal coordinates, collectively denoted by R. The potential ΔV varies in time as the trajectory changes with time.

In previous applications of the sudden limit to both the rotational and vibrational parts of the collision problem, the phase shift was determined by

$$\eta = -(2\hbar)^{-1} \int_{-\infty}^{+\infty} \Delta V dt. \qquad (2.33)$$

Here, ΔV depends only upon the trajectory, while the internal coordinates (for vibration and rotation) are independent of the time. For the relaxed sudden approximation, as given by Eq. (2.32), it is correct to say that the rotational coordinates are independent of time since any rotational contribution to the ω_{ij} appearing in Eq. (2.26) was set equal to zero. Then, since all of the rotational energy levels are degenerate, we can use any linear combination of wave functions to describe the rotational state. In particular, we can diagonalize ΔV and

η by using a set of Dirac delta wave functions in the internal rotational coordinates. For the vibrational case a similar diagonalization was carried out, but it is not clear that the vibrational coordinate can be treated as time-independent due to the exponential factor appearing in Eq. (2.27). However, ω was assumed to be a constant so that the diagonalization could be carried out; accordingly, we will assume that the internal vibrational coordinate is independent of time. Thus, the quantity ω in Eq. (2.27) will be used as a parameter to modify the results obtained previously, i.e., using Eq. (2.33) for three-dimensional atom-diatom scattering.

4. Interaction Potential

A problem facing any theoretical calculation of a collision process is how to choose an interaction potential which can at least exhibit the qualitative features of an experimental situation. The vibrational potential of the H_2 molecule is that of an anharmonic oscillator. The He + H_2 interaction potential should exhibit a shallow potential well. A purely repulsive nonspherical exponential potential is a reasonable approximation. Many interaction potentials of this analytic form have been introduced. We chose to use the potential fit of Krauss and Mies,[44] since it is the one adopted by Wartell and Cross.[15] It is more spherical and its anisotropy varies less rapidly as a function of the vibration coordinate than the more recent one of Gordon and Secrest, but it describes the essential features of the interaction quite well, especially in the highly repulsive range.

The Krauss-Mies interaction potential for the He + H_2 system is

given by

$$V(r,R,\gamma) = C \exp[- (\alpha_o - \alpha_1 R)r][A(\gamma) + B(\gamma)R] , \qquad (2.34)$$

where the H_2 displacement from the vibrational equilibrium is R, the distance from He to the bond center of H_2 is r, and γ is the angle between the molecular axis and the momentum vector. The numerical values of the constants are:

$$A(\gamma) = 1.1004[1 + 0.18250\ P_2(\cos\gamma)]$$

$$B(\gamma) = - 0.52151[1 - 0.27506\ P_2(\cos\gamma)]\ \text{a.u.}^{-1}$$

$$C = 198.378\ \text{eV} \qquad (2.35)$$

$$\alpha_o = 1.86176\ \text{a.u.}^{-1}$$

and

$$\alpha_1 = 0.3206\ \text{a.u.}^{-2}$$

where $P_2(\cos\gamma)$ is the second Legendre polynomial and all linear dimensions are given in atomic units (1 bohr = 0.529Å). This potential is valid for $2.5 \leq r \leq 3.8$ a.u. and $-1.4 \leq R \leq 0.6$ a.u.. Since the potential becomes large as R exceeds about 6 a.u., the exponential term involving R in Eq. (2.34) was expanded to first order in R which gave the potential used the form

$$V(r,R,\gamma) = C \exp[- \alpha_o r][1 + \alpha_1 Rr][A(\gamma) + B(\gamma)R]. \qquad (2.36)$$

The Legendre polynomial was written as a function of the angles θ, ϕ, θ, and Φ by use of the addition theorem for spherical harmonics. The relationship of these angles is shown in Fig. 1.

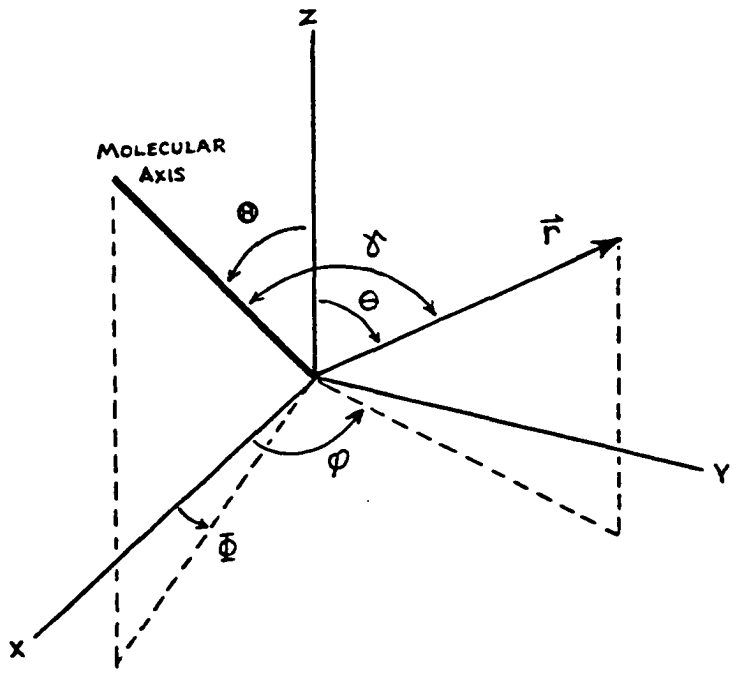

FIG. 1 Collision Geometry

CHAPTER III

DETAILS OF THE NUMERICAL COMPUTATIONS

For each energy and impact parameter a classical trajectory for the relative translational motion was calculated by integrating the classical equations of motion using the isotropic part of the interaction potential. This potential was obtained by averaging over the internal coordinates. The average over rotational coordinates was done in the standard manner by integrating over Θ and Φ. The average over the vibrational coordinates was carried out with a weight factor, $\exp[\alpha R^2]$, where α was chosen according to the identity of the diatomic molecule. The resulting trajectory was then expressed as a set of data giving the center of mass distance r and the scattering angle θ as functions of time. These functions were then used to obtain a time dependent interaction which followed the vibrational motion of the diatomic molecule.

The phase-shift calculations were made by integrating over the complete interaction potential for a given trajectory. The sudden-approximation results were obtained from the relation

$$\eta(E,b,R,\Theta,\Phi) = -(2\hbar)^{-1}\int_{-\infty}^{+\infty} V(r,\theta,\phi,R,\Theta,\Phi)dt. \qquad (3.1)$$

Here, E and b are the center of mass energy and impact parameter, respectively, R is the vibrational coordinate of the diatomic molecule, and Θ and Φ are the orientation angles for the diatomic molecule as de-

fined by Fig. 1. Phase shifts for the relaxed sudden approximation were calculated from a relation which differs from Eq. (3.1) only by the inclusion of an exponential factor, $\exp(i\omega t)$, under the integral. In Eq. (3.1), it was convenient to use the complete potential for the system rather than the anisotropic part, ΔV, which was used in the theoretical development. This substitution produced only a phase-factor difference in the scattering matrix elements and no difference in the transition probabilities, since $V(r,R,\theta,\phi) = V_o(r) + V(r,R,\theta,\phi)$ and since the matrix elements were obtained by integration over the internal coordinates. The trajectory was calculated for a spherically symmetric potential so the azimuthal angle ϕ was chosen to be zero.

The scattering matrix elements $S_{nn'}$ were obtained by integrating the exponential of the phase shift over vibrational wave functions of the molecule using the equation

$$S_{nn'}(E,b,\theta,\phi) = \langle n'|\exp(2i\eta)|n\rangle , \tag{3.2}$$

where $|n\rangle$ and $|n'\rangle$ are the initial and final states of the oscillator and were chosen as harmonic-oscillator wave functions. For this work, the initial vibrational state was chosen to be the ground state of the diatomic molecule. The transition probabilities, P_{on}, were obtained from the squares of the absolute values of the scattering matrix elements, i.e.,

$$P_{on}(E,b,\theta,\phi) = |S_{on}(E,b,\theta,\phi)|^2 . \tag{3.3}$$

Orientation-dependent cross sections Q_{on} were defined by and calculated from the relation,

$$Q_{on}(E,\theta,\phi) = 2\pi\int_0^{\pi} P_{on}(E,b,\theta,\phi)b\,db. \tag{3.4}$$

Finally, angle-averaged cross sections Q'_{on} for fixed energy were obtained by averaging over the internal angles of the diatomic molecule.

The calculations were performed for center of mass energies of 4, 5, 8, and 10eV. These energies fall within the range used in the quantum mechanical calculations of Secrest and Johnson for collinear collisions of the He and H_2 system.

Calculations were carried out on a PDP-10 system. Simpson's rule was used for all numerical integrations.

The values of ω to use in Eq. (2.27) for each energy were selected by calculating the elastic transition probability for various ω's and choosing those which gave values for the probability which was closest to the collinear calculation of Secrest and Johnson. The values used are given in Table I.

Table I. Values Selected for ω[a]

Collision Energy (eV)	ω (x $10^{14} s^{-1}$)
4	8.90
5	8.44
8	6.92
10	5.46

a. For H_2 as an harmonic oscillator $\omega = 8.28 \times 10^{14} s^{-1}$

Fig. 2A illustrates the behavior of the peak in the probability distribution as a function of the final state as ω becomes non-zero.

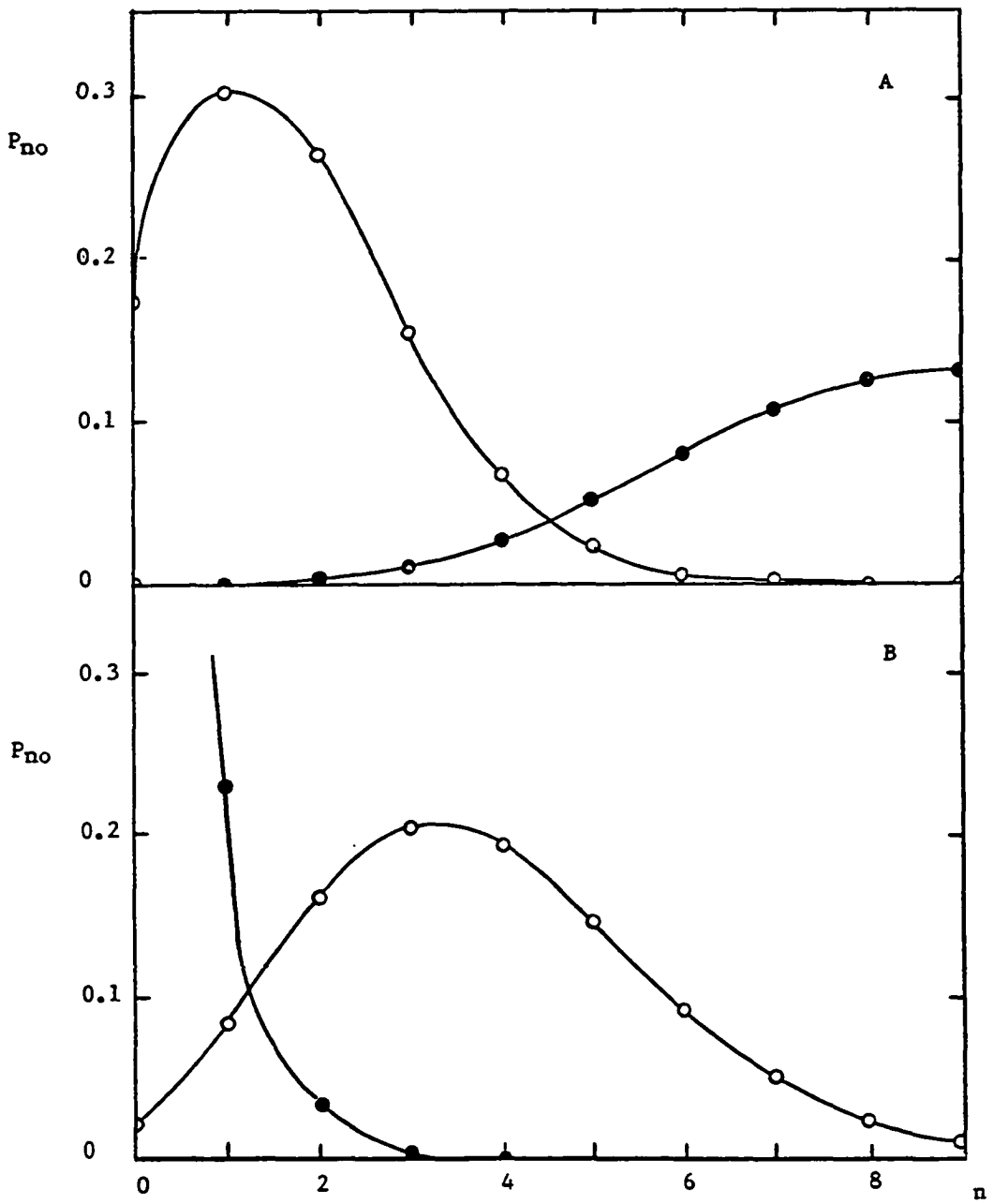

FIG. 2 Transition probability, P_{no}, vs. final state n for collinear collisions at zero impact parameter.
(a) 8eV Open circles for $\omega \neq 0$. Full circles for $\omega = 0$.
(b) Open circles for 10eV $\omega \neq 0$. Full circles for 4eV $\omega \neq 0$.

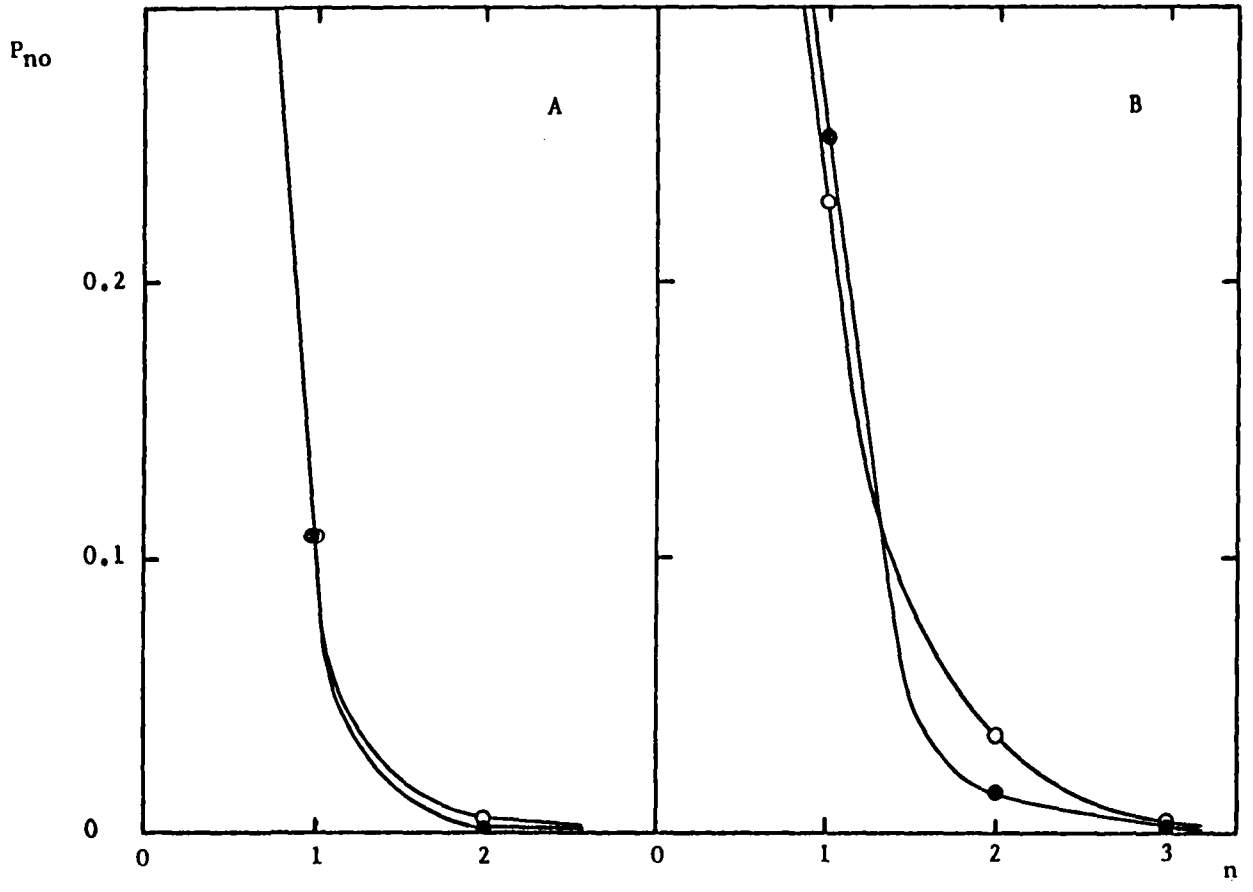

Fig. 3 Transition probability, P_{no}, vs. final state n for collinear collisions at zero impact parameter. Full circles represent the $\omega \neq 0$ results and the open circles represent the exact results of Ref. (10). (a) 4eV (b) 5eV

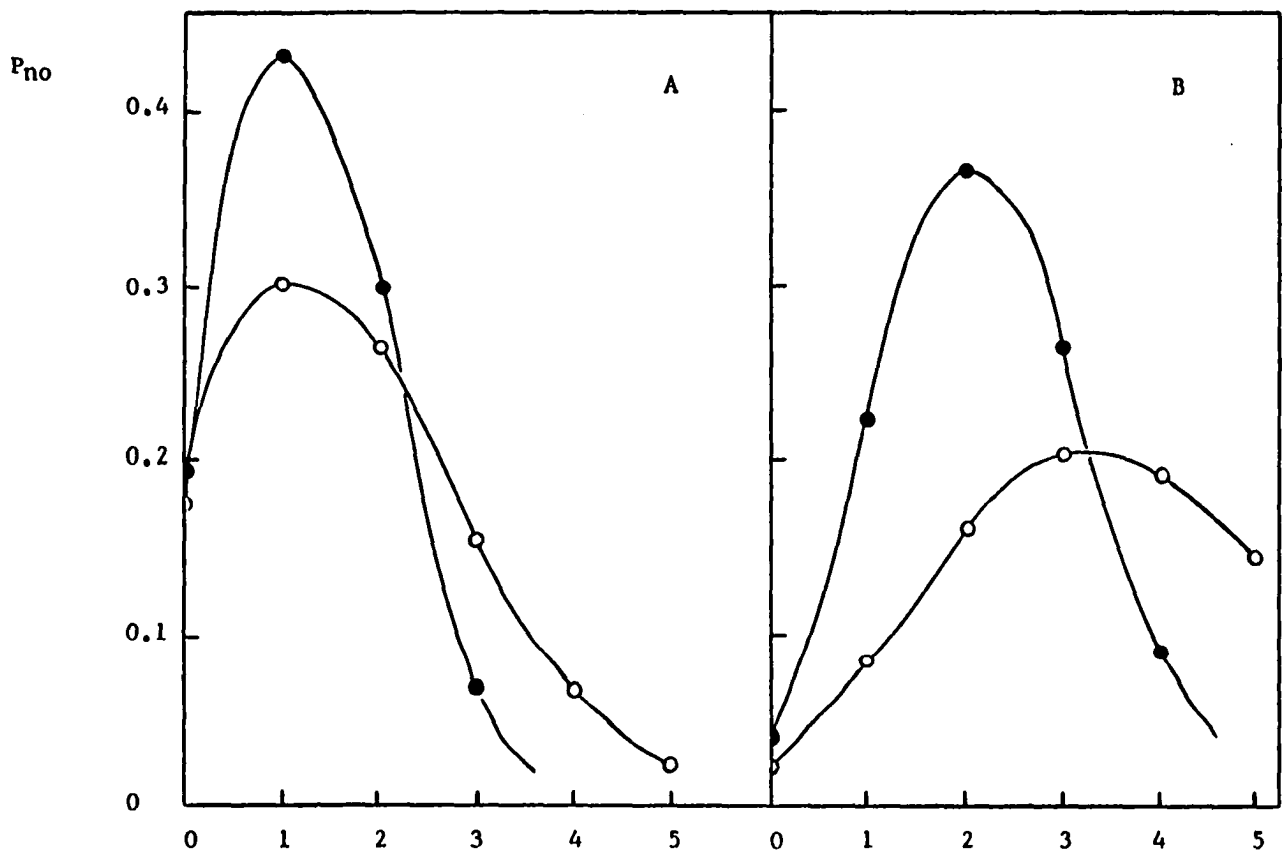

FIG. 4 Transition probability, P_{no}, vs. final state n for collinear collisions at zero impact parameter. Full circles represent the $\omega \neq 0$ results and the open circles represent the exact results of Ref. (10). (a) 8eV (b) 10eV

For a zero-impact parameter, collinear collision at 8eV, the $\omega = 0$ results are those of Wartell and Cross -- a broad distribution centered on relatively high final states. When ω is increased from zero the peak shifts to lower final states and the distribution becomes narrower. This result is an indication of how the sudden approximation overestimates the inelasticity of a collision process. For $\omega \neq 0$, the distribution spreads with increasing collision energy, giving significant transition probabilities at higher final states; i.e., the collision becomes more inelastic. This result is shown in Fig. 2B.

Comparisons of the collinear collision results of Secrest and Johnson with those of the present work are given in Figs. 3A through 4B. At 4eV the two results coincide with essentially no discernable difference, while at 5eV as n increases our values of P_{on} are slightly larger than the quantal results. The maximum in the probability distribution occurs for the same escited state for both results at 8eV, but the distribution for the relaxed sudden approximation is broader and significant values of P_{on} are seen at larger n. At 10eV the maximum for the present work has shifted to a higher n than the quantal result and the distribution is much broader.

Collisions for which the impact parameter is not zero exhibit more efficient transfer of energy when one end of the molecule is closest to the atom's projected trajectory. This effect is illustrated by Figs. 5 through 8 in which the sudden and relaxed sudden results are compared at 8eV as Θ is varied and Φ is kept constant. The elastic probability, P_{oo}, is smaller for the sudden approximation for all impact parameters. Each result shows a minimum for P_{oo} which occur near

the "aspect" of the molecule (equilibrium separation multiplied by $\sin\Theta$) presented to the colliding atom. As Θ is increased the minimum moves to larger impact parameter and the collision becomes more elastic as indicated by the increasing shallowness of the minimum. The relaxed sudden minimum more closely follows the aspect. At lower energy, the behavior is similar but the minima in P_{oo} are much shallower as shown by Fig. 9. The sudden approximation shows a larger range of impact parameters contributing to the inelastic scattering than does the relaxed sudden approximation. This range narrows as the energy of the collision decreases.

When both atoms of the molecule lie in a plane parallel to the incoming atom ($\Phi = \pi/2$) the relaxed sudden result rapidly approaches elastic scattering as Θ is increased and the range of impact parameters contributing to inelastic scattering narrows appreciably. The sudden result, however, indicates appreciable vibrational excitation for all values of Θ with the minimum in P_{oo} moving to larger impact parameter as Θ is increased. Also, a very broad range of impact parameters contributes to the inelastic scattering. This behavior is indicated by Figs. 10 through 13.

As shown in Fig. 14, where $\ln(Q_{no})$ is plotted against the final state n for four energies, the cross sections all fall off logarithmically with the rate of decrease less for higher energy. Fig. 15 compares the 8eV result with that obtained by the sudden approximation and we see that the sudden result falls off more slowly as the final state becomes higher.

A least squares fit to a parabola for the data in Table I yields

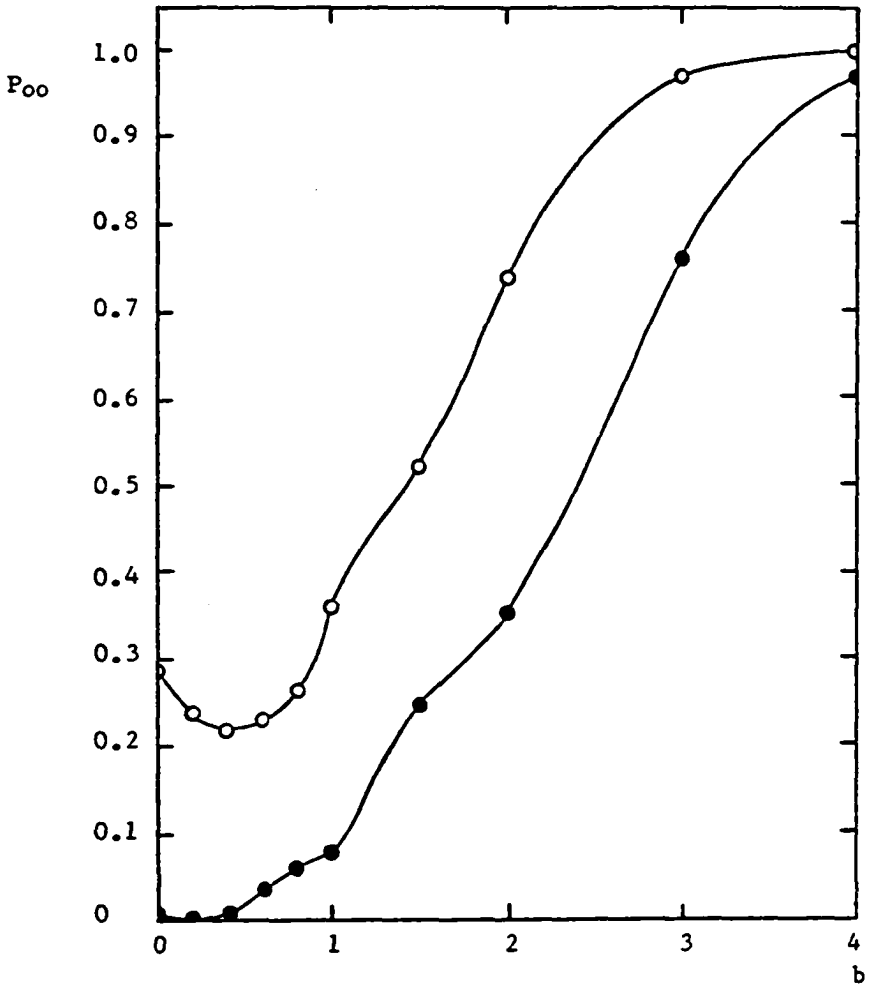

FIG. 5 Transition probability, P_{oo}, vs. impact parameter b at 8eV. o Relaxed approximation • Sudden approximation. Orientation angles for H_2 are $\theta = \pi/8$ and $\Phi = 0$.

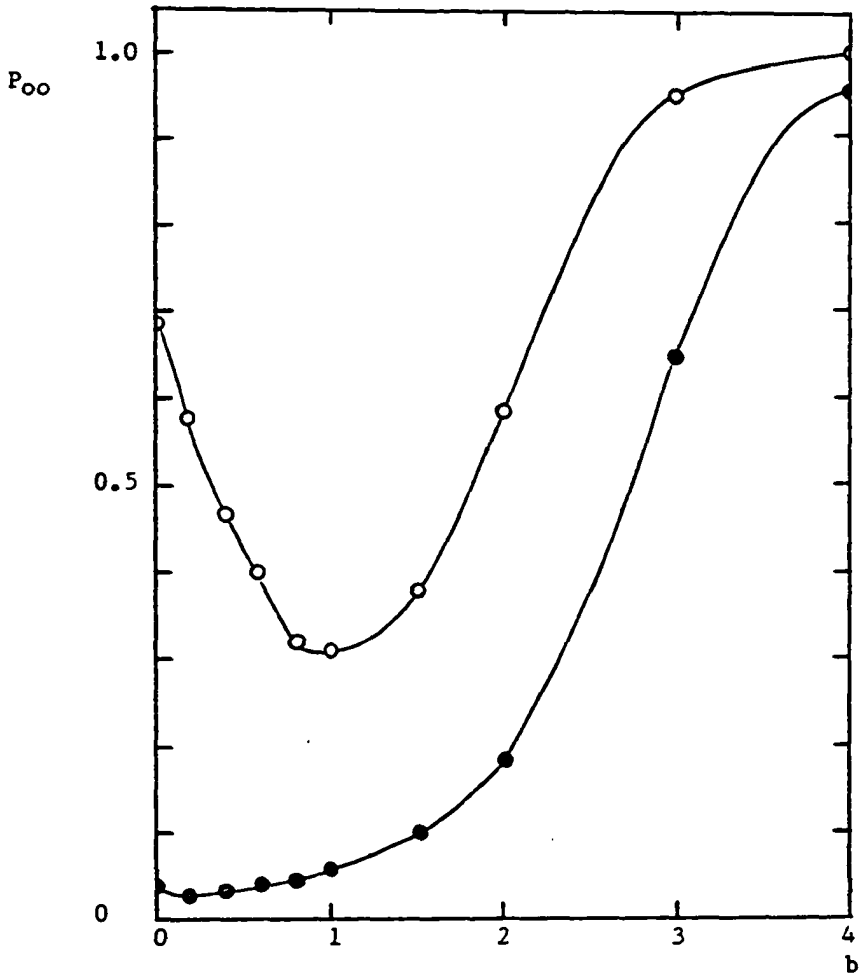

FIG. 6 Transition probability, P_{oo}, vs. impact parameter b at 8eV. o Relaxed approximation. • Sudden approximation. Orientation angles for H_2 are $\theta = \pi/4$ and $\phi = 0$.

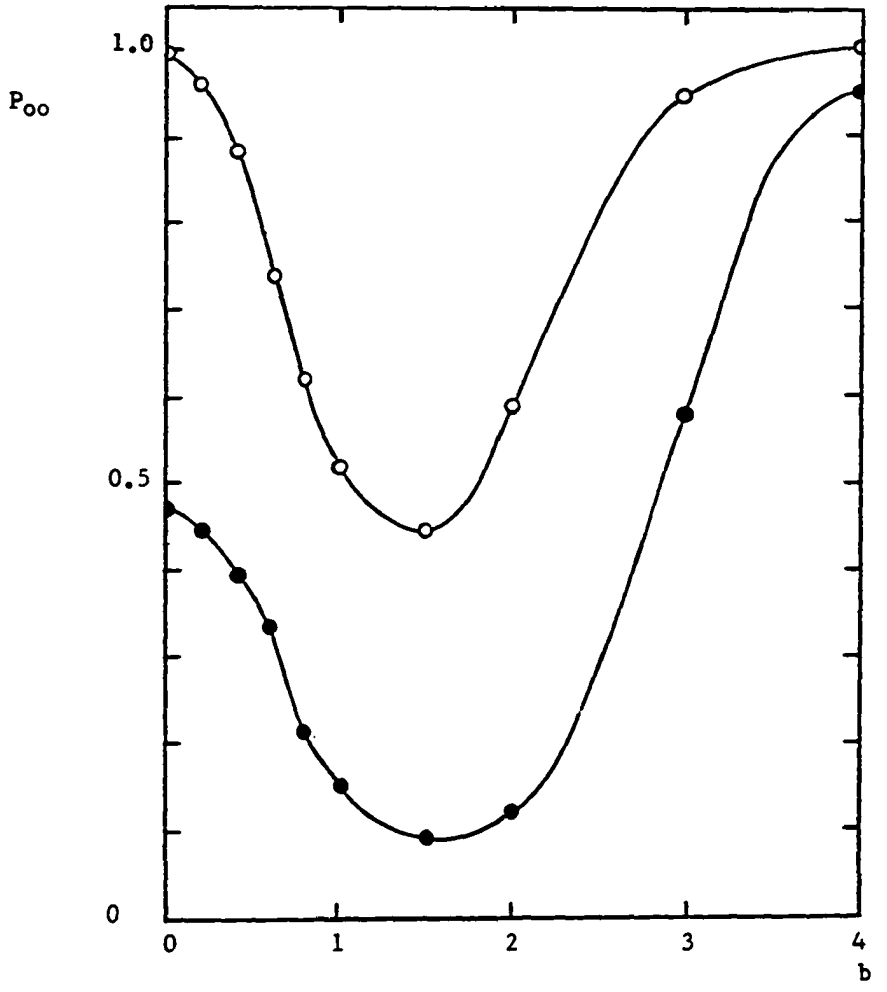

FIG. 7 Transition probability, P_{oo}, vs. impact parameter b at 8eV. o Relaxed approximation. • Sudden approximation. Orientation angles for H_2 are $\theta = 3\pi/4$, $\Phi = 0$.

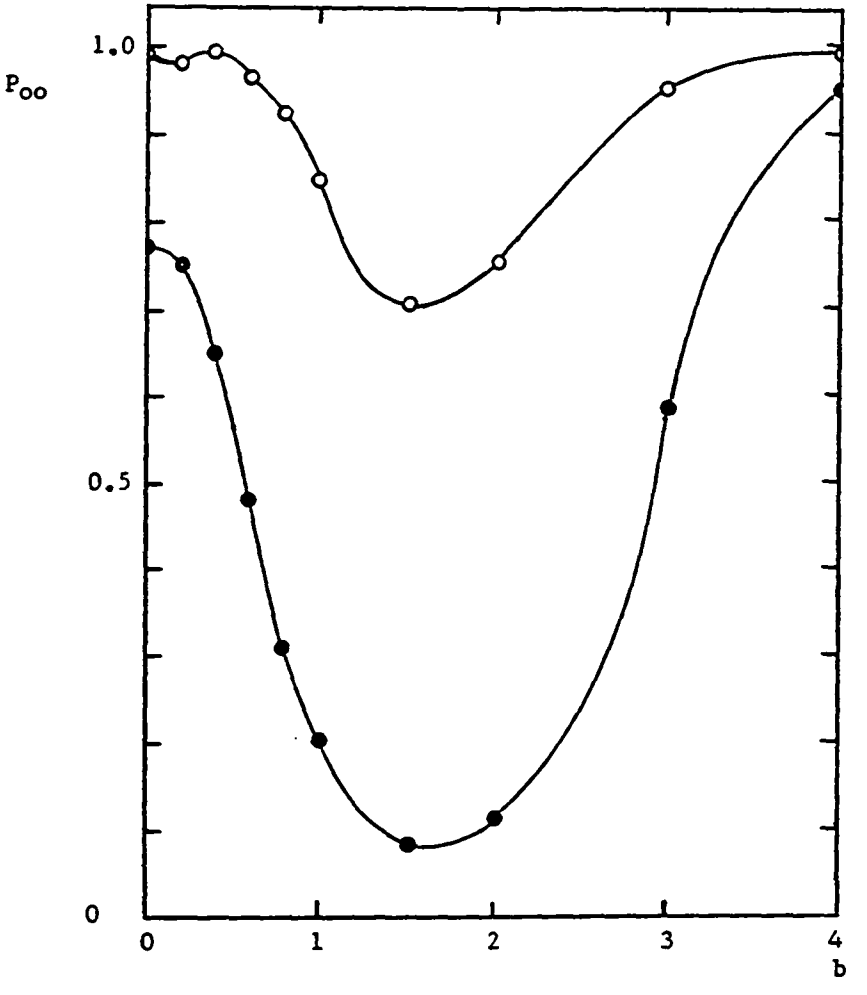

FIG. 8 Transition probability, P_{oo}, vs. impact parameter b at 8eV. o Relaxed approximation. • Sudden approximation. Orientation angles for H_2 are $\theta = \pi/2$, $\Phi = 0$.

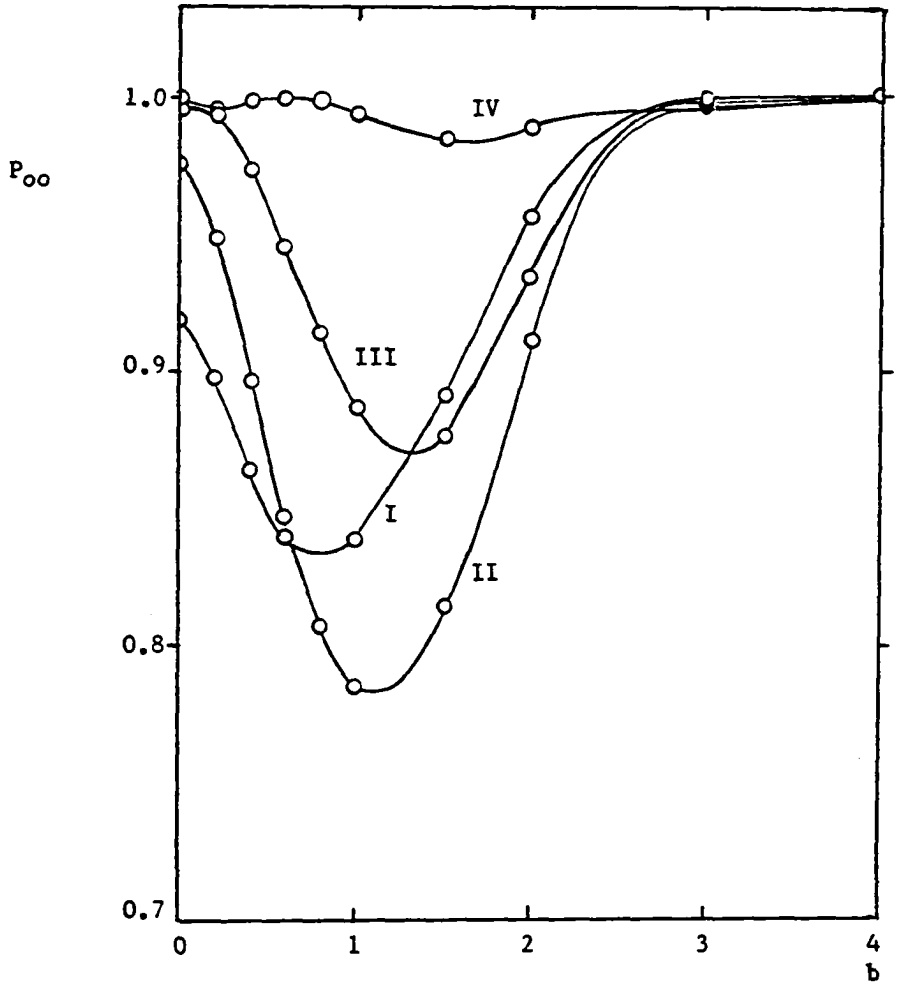

FIG. 9 P_{oo} vs. b for 4eV.
I: $\theta = \pi/8$, $\Phi = 0$ II: $\theta = \pi/4$, $\Phi = 0$
III: $\theta = 3\pi/8$, $\Phi = 0$ IV: $\theta = \pi/2$, $\Phi = 0$

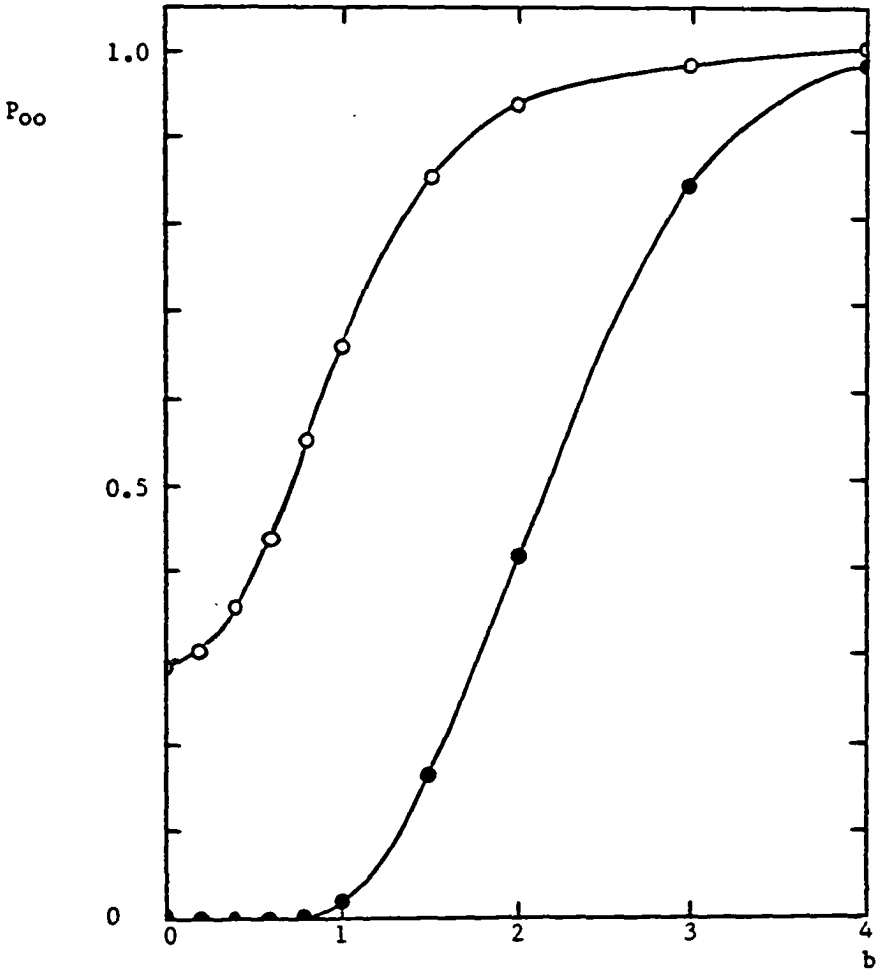

FIG. 10 P_{oo} vs. b at $\Theta = \pi/8$, $\Phi = \pi/2$
o 8eV relaxed. • 8eV sudden.

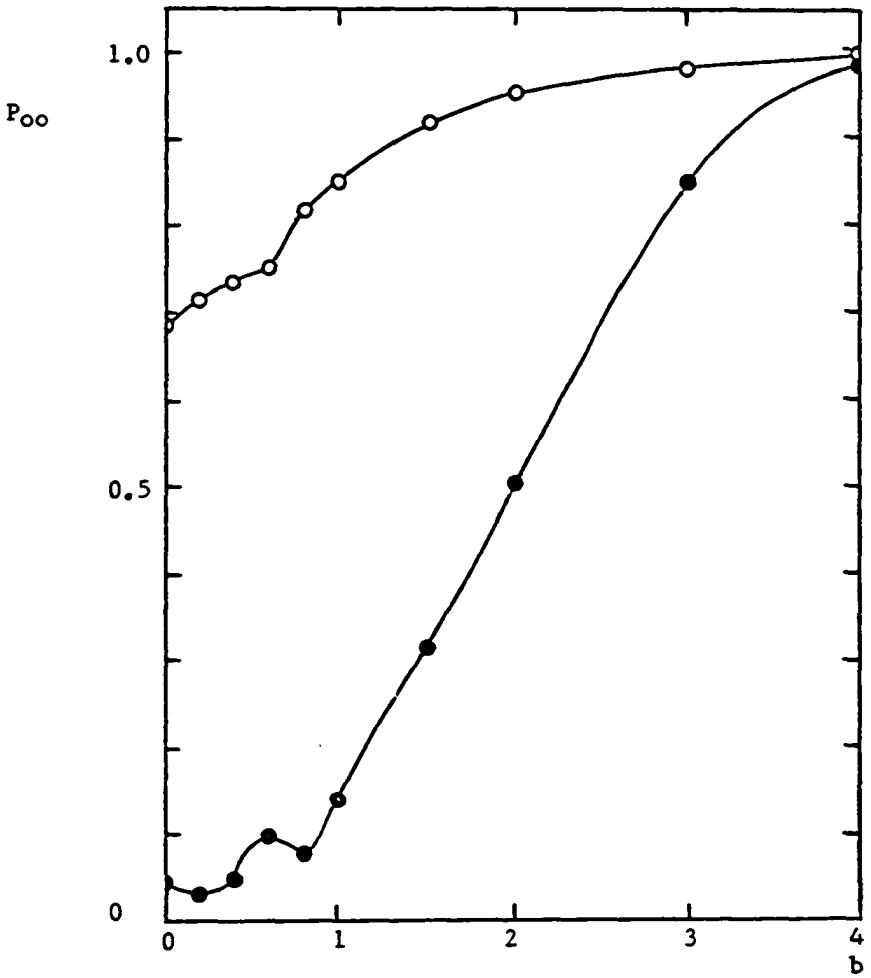

FIG. 11 P_{oo} vs. b for 8eV at $\theta = \pi/4$, $\phi = \pi/2$
o Relaxed • Sudden.

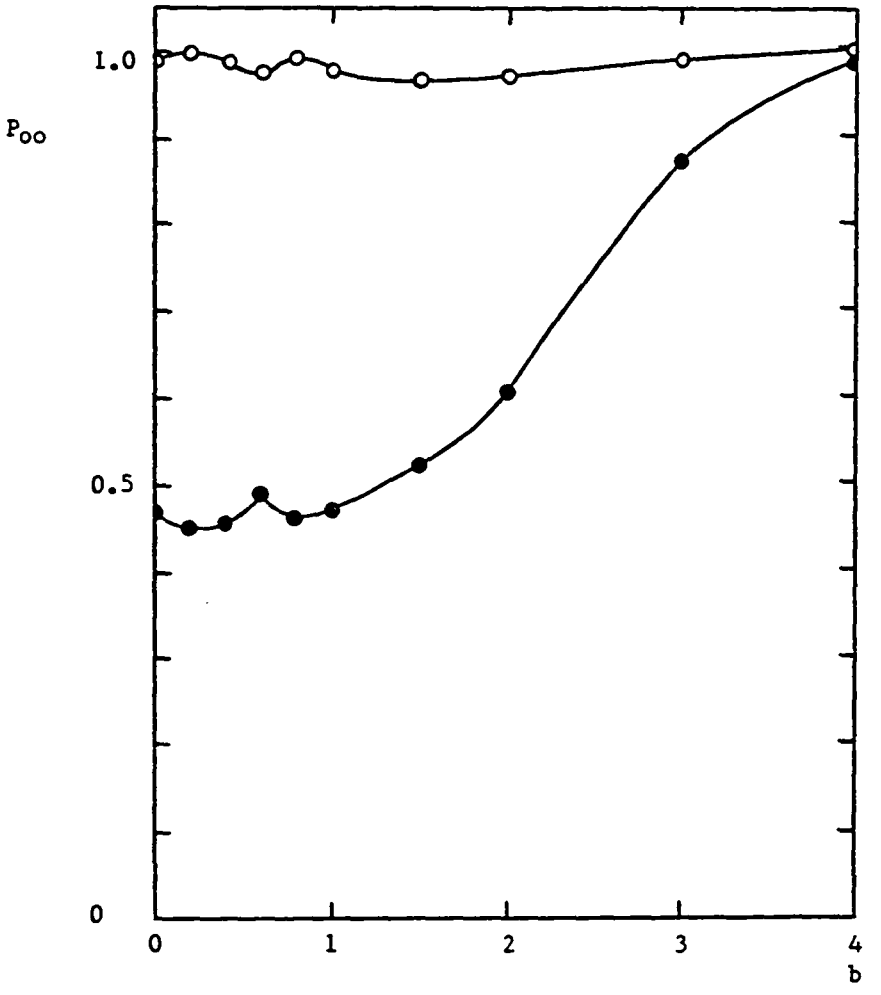

FIG. 12 P_{oo} vs. b for 8eV at $\theta = 3\pi/8$, $\phi = \pi/2$
o Relaxed • Sudden.

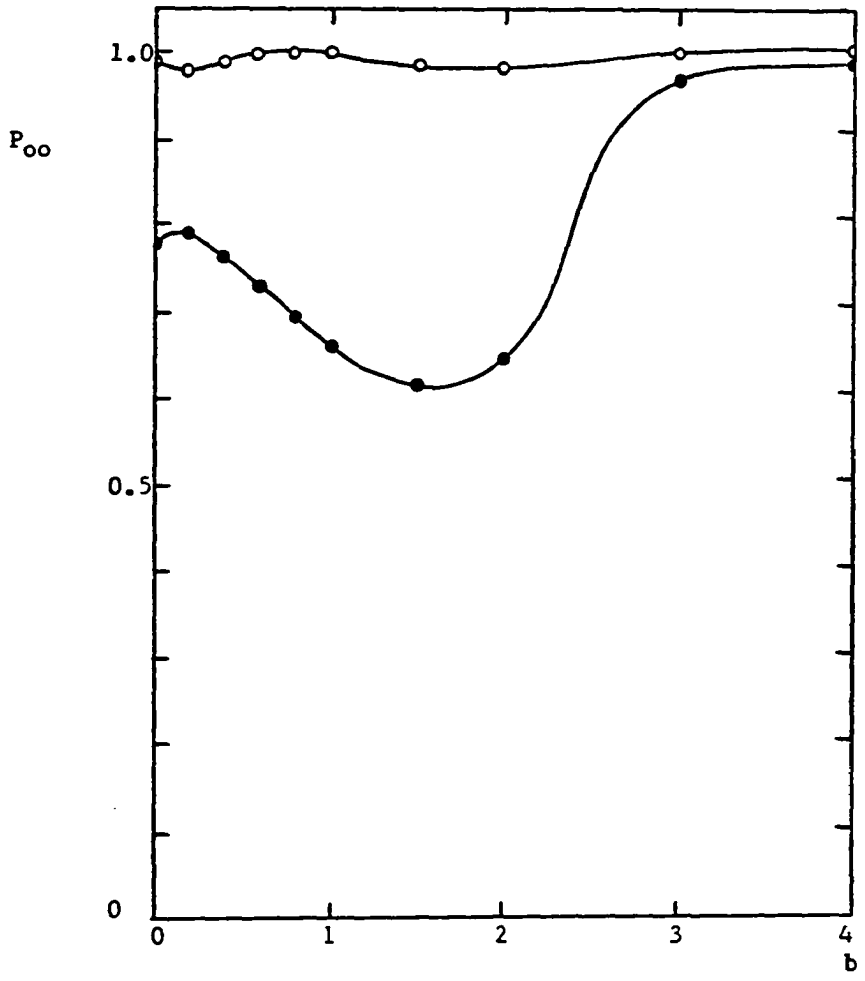

FIG. 13 P_{oo} vs. b for 8eV at $\theta = \pi/2$, $\Phi = \pi/2$
o Relaxed • Sudden.

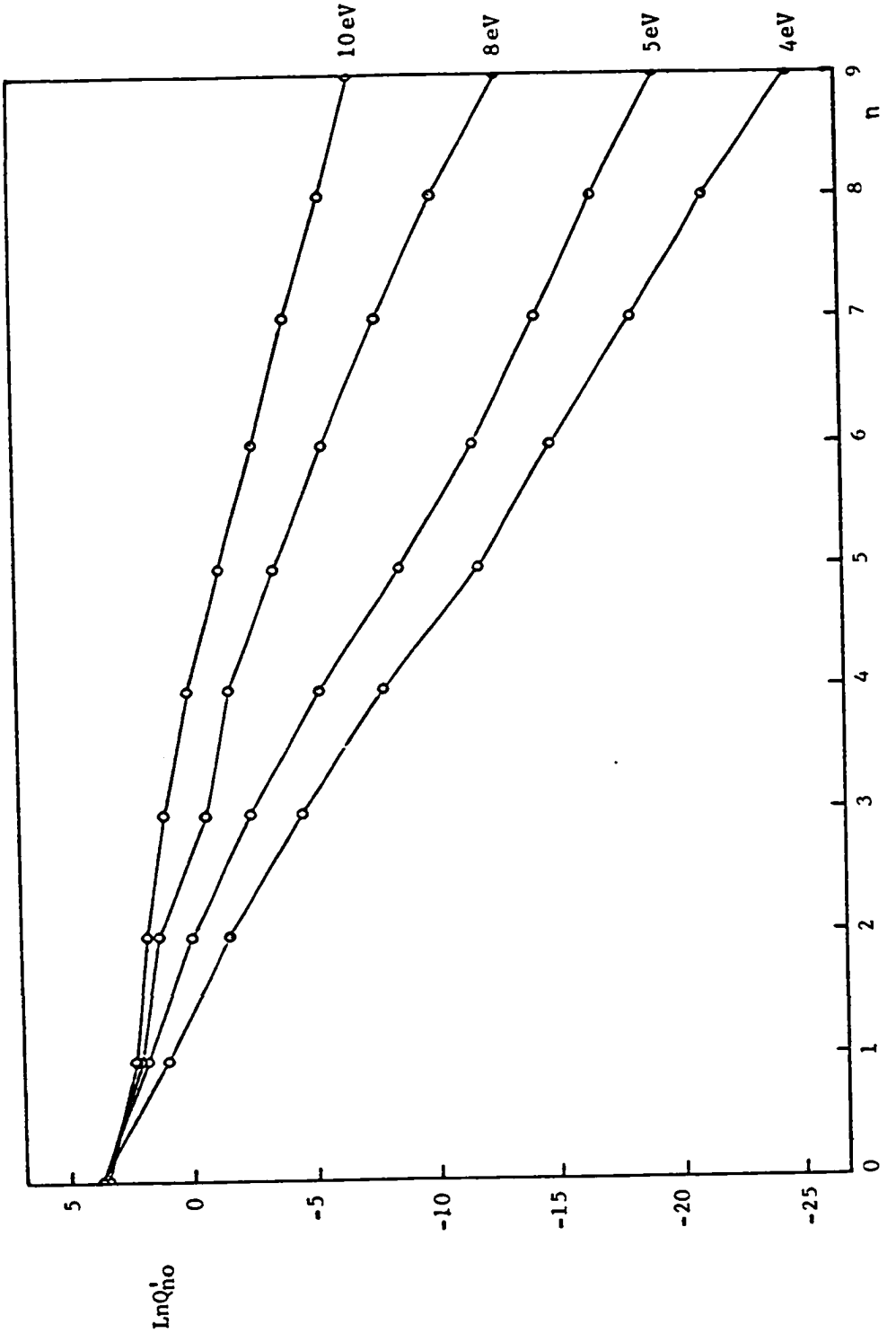

FIG. 14 Ln Q'_{no} vs. n

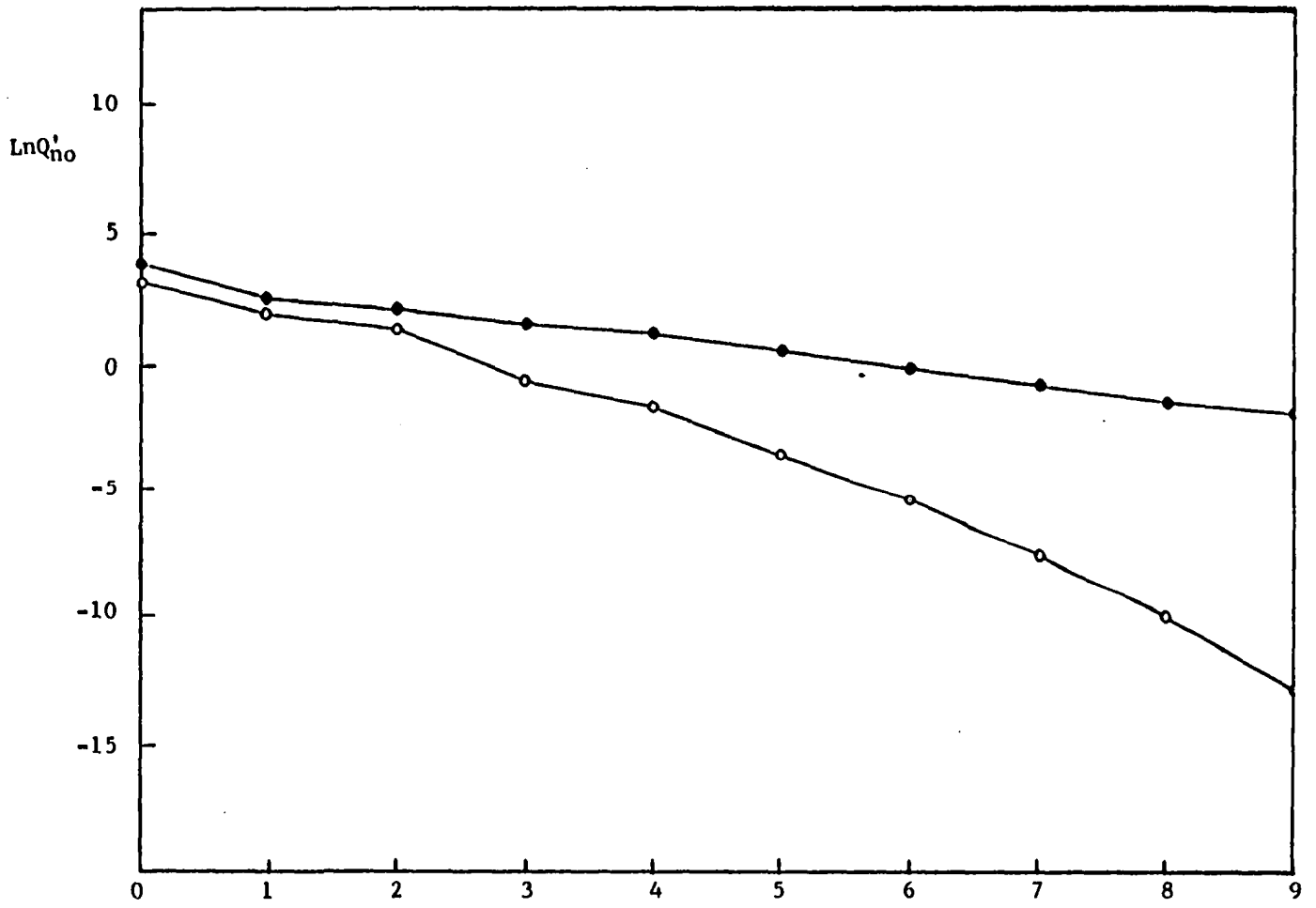

FIG. 15 Natural log of angle averaged cross section versus final state
o Relaxed sudden approximation. • Sudden approximation.

the curve,

$$\omega = \omega_o - aE - bE^2 \tag{3.5}$$

where

$$\omega_o = 9.73 \times 10^{14} s^{-1},$$

$$a = 6.42 \times 10^{12} eV^{-1} s^{-1},$$

and

$$b = 3.59 \times 10^{12} eV^{-2} s^{-1}.$$

The value of the center of mass energy for which $\omega = 0$ in Eq. (3.5) is 15.6eV. Thus, a lower limit for the application of the sudden approximation would seem to be a center of mass energy of about three times the dissociation energy for H_2. A straight-line fit to the same data yields a lower limit of about four times the dissociation energy.

CHAPTER IV

SUMMARY AND CONCLUSIONS

A three-dimensional semi-classical method using the relaxed sudden approximation has been developed and applied to vibrationally inelastic scattering of a structureless helium atom from a hydrogen molecule. A simple procedure was devised for selecting a value for ω which produced close agreement between the collinear semi-classical transition probabilities and the exact quantum mechanical values. The semi-classical method was then extended to three dimensions to obtain probabilities and cross sections for vibrational transitions from the ground state of an harmonic oscillator. These results were compared with those of the sudden approximation. A numerical lower limit on the collision energy was found for the use of the sudden approximation for the He + H_2 system.

For low center of mass energy, it was found that the exact result for the transition probabilities could be mimicked by a single choice of ω. At higher energies the relaxed sudden transition probabilities showed a tendency to peak at a higher vibrational state than those found by the exact quantal calculation.

While the sudden approximation indicates the general behavior of the probability peaks, it overestimates the contributions of higher vibrational states. The cross sections calculated from the probabilities

were smaller in the case of the relaxed sudden approximation. This behavior was expected since the relaxed sudden approximation introduced a more complicated energy dependence via the factor $\exp(i\omega t)$ which oscillates rapidly at low energies and reduces the transition probabilities. As the collision energy increases, the oscillations decrease with an attendant increase in the transition probability. It was also found that the region of significant inelastic vibrational scattering is restricted to a smaller range of impact parameters for the relaxed sudden approximation than for the sudden approximation. This range of impact parameters was centered around the aspect of the molecule and indicated that the most efficient energy transfer occurred when the incoming projectile approached one of the molecular atoms head-on. The restriction of significant vibrational scattering to a smaller range of impact parameters for the relaxed sudden approximation comes about due to the finite energy spacing introduced by ω. This means that stronger forces are necessary to produce vibrational transitions.

The values for ω were used to set an approximate lower energy limit of three to four times the dissociation energy on the use of the sudden approximation. Also, Eq. (3.5) could be used to determine values for ω within the energy range of this work although this was not done.

We would like to compare our three-dimensional calculation with experimental results and an exact three-dimensional calculation. So far, experiments for vibrational energy transfer in the He + H_2 system have been performed at energies below those considered in this work.[42] The same is true for theoretical calculations.[29] Wartell has performed sudden approximation calculations for the scattering of He from HD.[47]

It would be of interest to apply the relaxed sudden approximation to this system. Model calculations using this approximation could be extended to heavy partner collisions and more anisotropic potentials.

The method combines the numerical advantages of classical mechanics and rather simple techniques with which to handle the quantum properties of the system under investigation. It is easy to program and computing time is reasonable, although no attempt was made to produce a more efficient program. The number of trajectories needed is small — one for each set of b and E. Although actual physical values will ultimately rely on the full quantum description, we can use semi-classical means to reveal many details of the cross sections and probabilities. Even as new calculational techniques arise which will allow a full quantal description at moderate energies, a two-part approach will probably still be of value. In the low energy region, quantum mechanics will be used and in the high energy regime, semi-classical calculations can give an adequate description.

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